Accurate measurements of ozone absorption cross-sections in the Hartley band

In 2014, new measurements of the ozone absorption cross-section in the Hartley band were performed on gaseous ozone samples generated from a sample of purified liquid ozone. The cross-section at the 253.65 nm line of mercury was determined by comparison with an SRP.

UV laser - a stabilized Argon ion laser with three lines in the Hartley band was used to measure the optical density in the gas cell filled with low pressure ozone. The path length of the absorption cell was determined by interferometry.

Ozone generator - ozone was generated from oxygen by discharges and cryogenic trapping at 75 K. Ozone was purified after evaporation at 135 K, recondensation and evacuation of residual oxygen.

Purity analysis - possible impurities in the ozone sample were analyzed by mass spectrometry and Fourier Transform Infrared spectroscopy. Ozone purity was between 98.1% and 99.6% depending on the pressure.

Those new results, together with published papers on ozone cross section measurements at 253.65 nm, will be reviewed by a Task Group recently established by the Gas Analysis Working Group of the CCMQ (Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology).

This group is in charge of recommending a value and uncertainty for the ozone cross section at 253.65 nm to be used in ozone reference photometers and for comparisons of these standards in the on-going international comparison BIPM QM K1.

NO reacted measured by chemiluminescence, in line calibration with diluted NO standards validated during comparisons

NO2 gain measured by CAPS, in line calibration with diluted NO2 standards

FTIR analysis - HNO3 mole fractions at (0.2 to 1) µmol mol⁻¹ in standards at (10 to 40) µmol mol⁻¹.

O3 reacted measured by UV photometry, calibration with BIPM SRP

In parallel, a Gas Phase Titration (GPT) experiment was conducted, using the reaction of O₃ at the nmol/mol level with NO resulting in NO₂ and O₂. This allows measurements of O₂ anchored to NO and NO₂ standards of high accuracy produced by gravimetry.

Toxation scheme for ozone absorption cross-sections using Bogumil values as reference (Wavelengths plotted with a 0.2 nm shift from each other)

Ozone absorption cross-section values using Bogumil values as reference

Participants in comparisons of ozone standards coordinated by the BIPM

Relative N2O to NO reacted / NO2 gained to O3 reacted

Data used to deduce two other values of the absorption cross-section with expected uncertainty better than 1.8%.

From Viallon et al. Ozone cross-section measurements for gas phase titration submitted to Australian Chemistry on 23 August 2016.